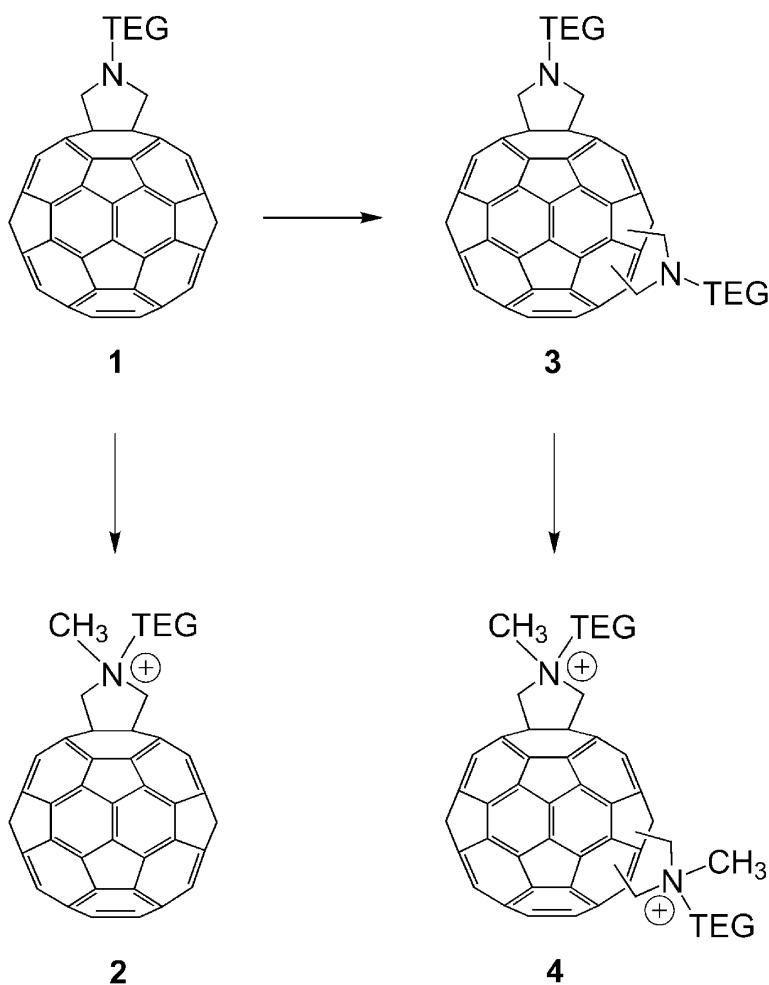Article

Modulation of the Reduction Potentials of Fullerene Derivatives

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Modulation of the Reduction Potentials of Fullerene Derivatives

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Abstract: The cyclic voltammetric (CV) study of a series of novel bisfulleropyrrolidines (**3**) and bisfullero-pyrrolidinium ions (**4**) is reported. The eight possible stereoisomers of each series were systematically investigated under strictly aprotic conditions that allowed the observation of up to four and five subsequent reversible reductions in **3** and **4**, respectively. Because of the stabilizing effect of positive charges, a significant enhancement of the electronegative properties was observed in **4**. In fact, **4**-*trans*-2 and **4**-*trans*-1 result among the strongest reversible electron-accepting C_{60} oligoadducts. Furthermore, the study evidenced that, in both **3** and **4**, the CV pattern, and in particular the potential separation between the second and third reductions, changes significantly with the addition pattern. A sequential π-electron model that simulates the effect of subsequent reductions of C_{60} bis-adducts gives a good correlation ($r > 0.96$) with the cyclic voltammetry data when the molecules are divided in two sets dependent on the location of the addends in the same or in opposite hemispheres.

Introduction

Fullerenes are excellent electron acceptors. In solution, up to 6 electrons can be reversibly injected into C_{60}, as shown by CV and differential pulse voltammetric studies.[1] C_{60} derivatives are generally more difficult to reduce than C_{60} itself, except for a few peculiar cases.[2] We have recently shown that the standard potential relative to reduction of fulleropyrrolidines can be modulated by alkylating the nitrogen atom in the fullerene-fused heterocycle (Scheme 1).[2a−c] Using fulleropyrrolidium salts (**2**), we were able to show that (1) these species are easier to reduce than fulleropyrrolidines and even than C_{60}: the reduction potential can be anticipated by up to 200 mV with respect to **1** and up to 50 mV with respect to C_{60}; (2) six reduction waves

Scheme 1
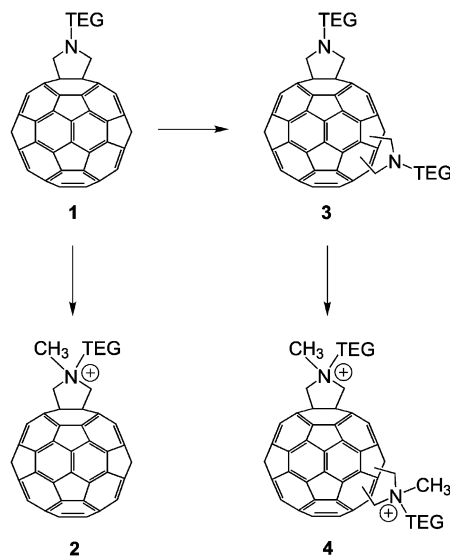
have been observed for the first time in fullerene derivatives using ultramicroelectrodes (Scheme 1).

It is generally accepted that the increase of the number of addends on C_{60} and higher fullerenes produces structural modifications that result in compounds progressively more difficult to reduce.[3] However, pulse radiolysis experiments indicate that bispyrrolidinium ions are even easier to reduce than mono fulleropyrrolidinium ions.[4]

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Scheme 2

cis-1
cis-2
cis-3
equatorial
trans-4
trans-3
trans-2
trans-1
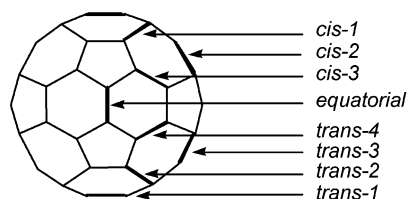
We report here a systematic voltammetric study of a series of novel compounds: neutral bispyrrolidines **3** and doubly charged bispyrrolidinium salts **4**. Additionally, we show that, at variance with previous reports on fullerene bis-adducts,[3] the CV morphology of bis-adducts changes with the addition pattern; in particular, the separation between the second and third reduction seems to be a rather sensitive probe of the relative location of addends onto the fullerene spheroid.

Results and Discussion

We have recently reported the isolation and characterization of all *N*-TEG bis-adducts **3** (Scheme 2).[5]

All of the bis-adducts were subjected to exhaustive alkylation by dissolving **3** in neat methyl iodide for 1 week.[2a] Each compound **4** consists of a mixture of stereoisomers. The two chiral nitrogen atoms give rise to four possible diastereoisomers, except in the case of **4**-*trans*-1 where meso structures are possible, which lead to only two diastereoisomers. The electrochemical studies were performed on the mixture of isomers. All of the bis-salts are reasonably soluble in THF.

Electrochemistry. In THF solutions, at 25 °C and under very dry conditions,[6] fulleropyrrolidine bis-adducts **3** undergo four reversible one-electron reduction processes, as exemplified in Figure 1, where the CV curves for **3**-*cis*-3, **3**-*trans*-4, **3**-*trans*-1, and **3**-*trans*-2 are displayed. The $E_{1/2}$ values relative to the four reductions of all eight stereoisomers are collected in Table 1.

The CV patterns of bis-adducts are reminiscent of that of *N*-TEG monoadduct **1** which however also undergoes, under the same conditions, a fifth reversible reduction at more negative potentials (Table 1).[7] In the case of bis-adducts **3**, by contrast, a further reduction was not detected even within the wider negative potential window investigated at low temperature (down to −3.2 V at −60 °C), as shown, for **3**-*trans*-1, in Figure 2. Comparison of the $E_{1/2}$ values for the first reduction of bis-adducts **3** with that of the monoadduct **1** (Table 1) shows that the former are in general more difficult to reduce than the latter: the negative shift of the corresponding $E_{1/2}$ value with
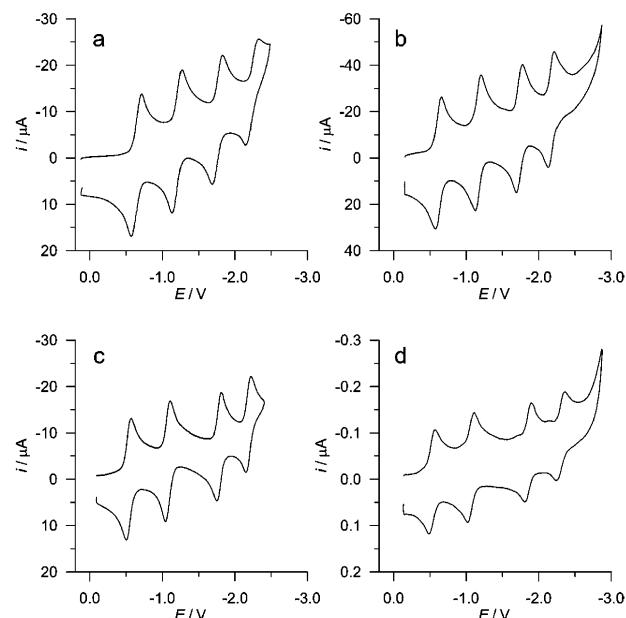
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Figure 1. CV curves of 0.5 mM (a) **3**-*cis*-3; (b) **3**-*trans*-4; (c) **3**-*trans*-1; (d) **3**-*trans*-2, THF solutions (0.05 M TBAH). Scan rate: (a) and (c) 0.5 V/s; (b) 2 V/s; (d) 10 V/s. Working electrode, Pt wire or (d) Pt disk electrode (diameter = 125 μm). T = 25 °C.

Table 1. $E_{1/2}$ Values (V vs SCE, T = 25 °C) Relative to Subsequent Reductions of the Eight Stereoisomers of *N*-TEG-fulleropyrrolidine Bis-adducts **3** and Parent Compounds, C_{60} and **1**

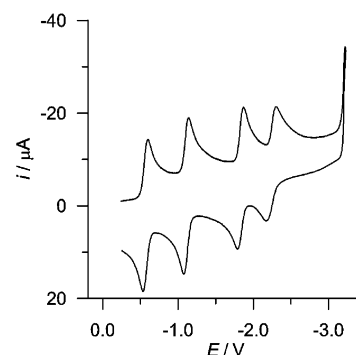| species	$E_{1/2}$/V				
C_{60}	−0.35	−0.94	−1.50	−1.99	−2.50
1	−0.44	−0.99	−1.60	−2.10	−2.83
3-*trans*-1	−0.51	−1.05	−1.76	−2.18	
3-*trans*-2	−0.53	−1.06	−1.85	−2.30	
3-*trans*-3	−0.60	−1.14	−1.84	−2.26	
3-*trans*-4	−0.61	−1.16	−1.74	−2.18	
3-equatorial	−0.62	−1.15	−1.85	−2.30	
3-*cis*-3	−0.64	−1.20	−1.76	−2.24	
3-*cis*-2	−0.65	−1.18	−1.85	−2.31	
3-*cis*-1	−0.56	−1.10	−1.84	−2.31	

Figure 2. CV curve of 0.5 mM **3**-*trans*-1 THF solution (0.05 M TBAH). Scan rate: 0.5 V/s. Working electrode: Pt wire. T = −60 °C.

respect to monoadduct ranges from 70 mV for **3**-*trans*-1 to 210 mV for **3**-*cis*-2. Such a trend, also observed for the subsequent reductions, is expected on the basis that saturation of the second double bond makes bis-adducts worse electron acceptors than monoadduct.

It is worth noticing, however, that the shift of each reduction in **3** with respect to the corresponding process in **1** is not constant along the series of stereoisomers.
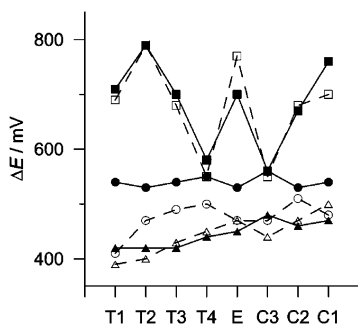
Figure 3. Potential gaps (ΔE, absolute values) between subsequent redox processes in bisfulleropyrrolidine **3** (full lines) and bisfulleropyrrolidinium **4** (dashed lines): ($\bullet$, and $\circ$) $E_{1/2}^{II}-E_{1/2}^{I}$; ($\blacksquare$ and $\square$) $E_{1/2}^{III}-E_{1/2}^{II}$; ($\blacktriangle$ and $\triangle$) $E_{1/2}^{IV}-E_{1/2}^{III}$.
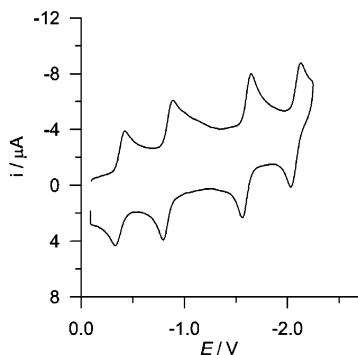

Figure 4. CV curve of a saturated **4**-equatorial THF solution (0.05 M TBAH). Scan rate: 0.5 V/s. Working electrode: Pt wire. $T = 25\ °C$.

Isomers **3**-*cis*-3 (Figure 1a) and **3**-*trans*-4 (Figure 1b), for instance, closely resemble C_{60} because their regular, evenly spaced CV curve differs from that of the parent fullerene uniquely for its location on the potential axis. By contrast, **3**-*trans*-2 (Figure 1d) shows a gap between the second and third reductions that is significantly larger than that in the above isomers and in both C_{60} and **1** (compare Table 1).

These findings are summarized in Figure 3, where the gaps between subsequent reductions for all isomers are shown. The gap between the first and second reduction is almost constant along the series and amounts to about 530−560 mV, close to the values found in C_{60} (590 mV) and **1** (550 mV). Also, the gap between the third and fourth reduction is rather constant (420−480 mV) and slightly smaller than the corresponding value in C_{60} and **1** (490−500 mV). Conversely, the gap between the second and third reductions changes rather sharply along the series: the narrowest gap is found in the case of **3**-*cis*-3 (560 mV), identical to the value found in C_{60}, while the widest one is that of **3**-*trans*-2 (790 mV).

Similar results were obtained for the charged *N*-methyl-*N*-TEG-fulleropyrrolidinium bis-adducts **4**. The rather lower solubility in THF of these compounds with respect to the neutral fulleropyrrolidines, along with adsorption phenomena and partial chemical instability of multiply reduced species, made in general the analysis of the CV curves of **4** more difficult than in the previous case. Similar to their neutral counterparts, all eight stereoisomers show four reversible one-electron reductions at 25 °C, as illustrated in Figure 4 for isomer **4**-equatorial. The $E_{1/2}$ values for all redox processes are reported in Table 2.

At low temperature (−60 °C), a fifth reduction, partially reversible, was also observed, as shown in Figure 5 for isomers

Table 2. $E_{1/2}$ Values (V vs SCE, $T = 25\ °C$) Relative to Subsequent Reductions of the Eight Different Stereoisomers of Bis-*N*-methyl-*N*-TEG-fulleropyrrolidinium Bis-adducts **4** (Iodide Salts) and Parent Compound **2**[a]

species	$E_{1/2}$/V					
2	−0.29	−0.79	−1.34	−1.84	−2.66[a]	−3.15[a]
4-*trans*-1	−0.26	−0.67	−1.36	−1.75	−2.42[a]	
4-*trans*-2	−0.27	−0.74	−1.53	−1.93	−2.60[a]	
4-*trans*-3	−0.34	−0.83	−1.51	−1.94	−2.63[a]	
4-*trans*-4	−0.33	−0.83	−1.38	−1.83	−2.67[a]	
4-equatorial	−0.36	−0.83	−1.60	−2.07	−2.65[a]	
4-*cis*-3	−0.38	−0.85	−1.40	−1.84	−2.70[a]	
4-*cis*-2	−0.33	−0.84	−1.52	−1.99	−2.67[a]	
4-*cis*-1	−0.34	−0.82	−1.52	−2.00	−2.66[a]	

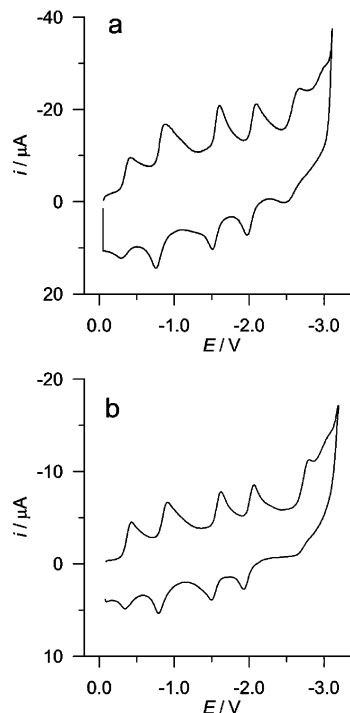[a] Data obtained at −60 °C.

Figure 5. CV curves of a saturated (a) **4**-equatorial; (b) **4**-*trans*-3, THF solutions (0.05 M TBAH). Scan rate: (a) 2 V/s, (b) 0.5 V/s. Working electrode: Pt wire. $T = -60\ °C$.

4-equatorial and **4**-*trans*-3. The reversibility of such a process increased, that is, anodic-to-cathodic peak current ratios were closer to one, when the scan rate was increased, and therefore it was safely attributed to the fifth reduction of the fullerene spheroid. Conversely, a sixth peak that is observed at slightly more negative potentials (Figure 5) could not be attributed to the starting species because its height decreased as the scan rate was increased, and it was rather attributed to a follow-up product of the partly irreversible fifth reduction. As a likely consequence of the stabilizing effect of the two positive charges in the methylated bis-adducts,[2a−c] the first reductions of **4**-*trans*-2 and **4**-*trans*-1 are even easier (by 20 and 30 mV, respectively) than those in monoadduct **2** (Table 2).

Incidentally, this places these charged isomers among the strongest reversible electron-accepting C_{60} derivatives, being anticipated with respect to C_{60} itself by 80 and 90 mV, respectively. Inspection of the $E_{1/2}$ values reported in Table 2 shows that also, in the case of the methylated bis-adducts **4**, a nonconstant gap is observed between the second and third reduction (Figure 3). The average gap between the first and

second reduction is in fact 570 mV, close to the corresponding values observed for C_{60} and **2**. However, while for the latter species a similar value is also measured between the second and third reduction, the gap varies in the case of bis-adducts, from 530 to 550 mV (**4**-*trans*-4 and **4**-*cis*-3) up to 770 mV (**4**-equatorial).

The effect on the potential gaps between subsequent reductions in the various isomers may help to elucidate the role of the addends and of their relative locations on the electronic properties of bis-adducts.

It is well known that the regular, evenly spaced six-reduction CV pattern as observed in C_{60} and C_{70} is usually lost in their derivatives. Because of molecular features such as electronic coupling and HOMO–LUMO gaps, the redox potentials ($E_{1/2}$) of subsequent electron transfers to discrete molecules are generally not evenly spaced.[8] However, when such molecular effects are absent, such as for instance in C_{60}, a linear variation of $E_{1/2}$ with the valence state of the molecule is observed, as predicted by the Born theory.[9,10] In fullerene monoadducts such as methanofullerenes and fulleropyrrolidines, a larger gap between the fourth and fifth reductions is found with respect to the previous ones due to the partial removal of LUMO degeneracy.[2a–c,10] Such an effect, together with the negative shift of the redox processes usually observed in fullerene derivatives, explains why only five reductions are observed, the sixth reduction becoming too negative to be observed in the available negative potential windows. Vice versa, in *N*-methyl-*N*-TEG-fulleropyrrolidinium ion monoadduct **2**, because of the anticipation of all reduction processes due to the stabilizing effect of the positive charge, one observes the occurrence of such a sixth reduction.[2a–c] For the same reasons, the fifth reduction cannot be observed in the case of *N*-TEG-fulleropyrrolidine bis-adducts **3** (Figure 2) but may be observed after methylation of the N atoms (Figure 5).

Figure 3 shows that the gap between the second and third reduction depends strongly on the nature of the bis-adduct. To obtain a deeper understanding of such a rather unexpected aspect of voltammetric behavior of this class of compounds, quantum chemical calculations were therefore carried out.

Calculations. Both empirical considerations and quantum chemical AM1 calculations failed to reproduce the experimental differences. The gaps do not correlate with simple molecular descriptors such as the distance between the two addends. The AM1 calculations showed that the observed reduction potentials do not correlate with (a) the heat of formations of the reduced species, (b) the LUMOs energies of the neutral molecules, (c) the orbital energies of the reduced systems, or (d) other descriptors, connected to the π-electron conjugation pattern, that have been used before to rationalize the nonlinear optical response in fullerene derivatives.[11]

In the past, many electronic properties of C_{60} have been described by the simplest possible quantum chemical approach, the Hückel theory. For instance, the molecular orbital pattern of C_{60} was successfully predicted by Raghavachari.[12] More

recently, Fowler was able to predict the halogen addition pattern in $C_{60}X_6$ (X = Cl, Br) and $C_{70}Cl_{10}$[13] with a simple extension of the Hückel model based on ideas developed by Coulson.[14,15] Here, we use a similar approach that employs the molecular orbitals to calculate the free-valence index, F_r. It originally served to rationalize the radical addition to small unsaturated hydrocarbons[14,15] and is defined as

$$F_r = N_{max} - N_r \qquad (1)$$

where N_r is the sum of bond orders over all bonds joining atom r to the remainder of the π system. N_{max} is the maximum value of this sum and depends on how many other trivalent carbons are attached to the atom in question; N_{max} is $\sqrt{m}$ for a trivalent carbon attached to m other π atoms.[16] We simply calculate the electrostatic interactions between the atoms that host the first two reductions, selected on the basis of F_r, and that (or those) where the third electron will be mainly located. The site(s) of first reduction is calculated on the basis of a 56-center, 56-electron system. The site(s) of second reduction is recalculated on the basis of a 56-center, 57-electron system. The first and second reductions have a total charge of −1 each. The third site(s) − recalculated on the basis of a 56-center, 58-electron system − is assumed to contain only a fractional charge, proportional to F_r divided by the number of symmetry equivalent atoms. The role of the fractional charge is to assist or to discourage accommodating the incoming third electron. The electrostatic interaction between the first two electrons and the residual charge estimates how easy or difficult is to have a third reduction. In practice, the larger is the value of the electrostatic interaction, the more difficult it is to introduce the electron, and a larger reduction potential is required.

Figure 6 shows the eight Schlegel diagrams of the bisfulleropyrrolidines with the sites of the two pyrrolidine adducts, and the three reductions. Two rules must be specified: (1) If two or more sites have the same F_r, the electronic charge is split equally over the number of sites, unless (2) another reduction is competing for the same sites, in which case the charge is localized (as little as possible) to avoid the interaction of two different electrons on the same atom.

The rules are best illustrated by considering practical cases: (a) in *cis*-2, *cis*-3, *trans*-2, *trans*-3 adducts, the first two electrons enter the same sites, or atomic orbitals, and it is natural to assume that each will take one; (b) analogously, in the equatorial and *trans*-4 bis-adducts, the second and third reductions occupy the same sites, and it is assumed that one will take the electron and the other will "nest" the following reduction; (c) in *cis*-1, the first electron enters two sites, and the second enters a different one. The two equivalent sites of first reduction each take one-half of the electronic charge. The site of second reduction takes the full electronic charge; (d) *trans*-1 bisfulleropyrrolidine is a complicated case. The four equivalent sites of the first reduction each take one-quarter of the electronic charge. The 4 atoms for which the second and third reductions compete localize each reduction in a pair of sites in five

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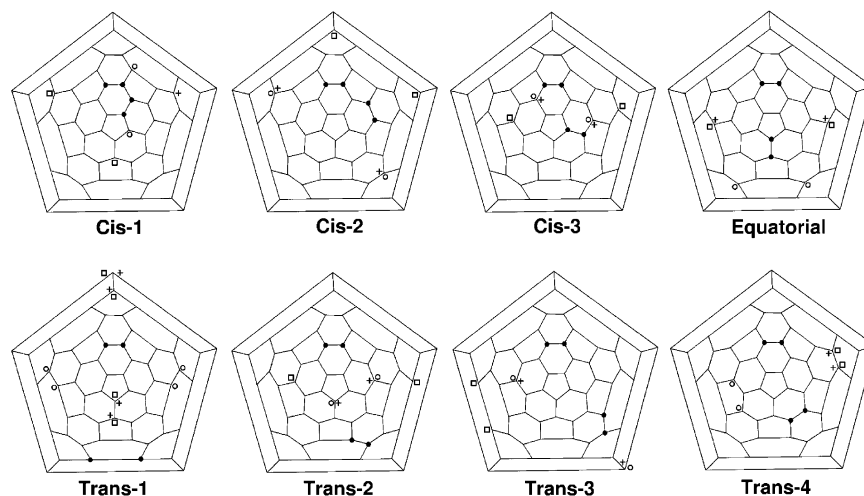
Figure 6. Schlegel diagrams with the location of the two pyrrolidine rings (●), the site(s) of the first (○) and second (+) and third (□) reductions.
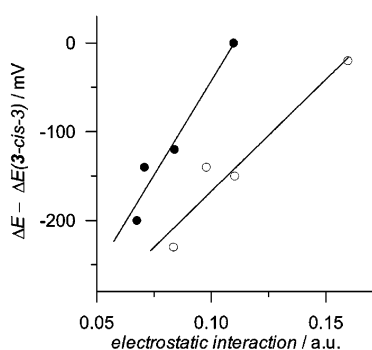

Figure 7. Correlation between the potential differences of the second and third reduction of **3** (referred to **3**-*cis*-3) and the calculated electrostatic interaction: (●) cis and equatorial bis-adducts, (○) trans bis-adducts.

resonance structures. The final electrostatic interaction is taken as an average of the contribution of each structure (other choices, based for instance on only three resonant structures, gave similar results).

As can be seen in Figure 6, all sites calculated with F_r for the reductions are at least doubly degenerate for symmetry reasons. The charge is thus divided over the centers according to rules 1 and 2. Once the electrostatic interactions were calculated and compared to the differences of the reduction potentials between the second and the third reduction, it became evident that the eight molecules split into two sets.

Figure 7 illustrates the trends which have correlation coefficients of 0.97 for the set made by the bis-adducts with addends located in the same hemisphere (*cis*-1, *cis*-2, *cis*-3, and equatorial) and 0.96 for the set of molecules that includes addends located in opposite hemispheres (*trans*-1, *trans*-2, *trans*-3, and *trans*-4).

The success of the model implies that the gaps between the second and third reduction have a dominant electrostatic contribution that is due to the way the addends modify the molecular orbitals by saturating the π-electron system of C_{60}. The separation of the molecules in two sets, where the pyrrolidines are located in the same or in the opposite hemisphere, is rather interesting and can be qualitatively explained considering that the derivatization introduces small local positive charges at the tetravalent saturated carbons. When the positive atoms of the addends are closer, they can interact

with the incoming negative charge more strongly and promote more easily the reduction.

Conclusions

In this paper, we report the standard potentials relative to the subsequent four and five reversible reduction processes respectively occurring in two series of bis-adducts of C_{60}, neutral bispyrrolidines **3** and bis-salts **4**. Both series show similar trends, the bis-salts showing a more electronegative behavior, as expected on the basis of previous work. Some isomers have a rather unexpectedly wide potential difference between the second and third reductions. In an attempt to rationalize this behavior, we have performed quantum chemical studies. This work indicates that the experimental results can be simply explained with a sequential π-electron model whose main features have been used in the past to predict the halogen addition pattern in $C_{60}X_6$ (X = Cl, Br) and $C_{70}Cl_{10}$.

Experimental Section

Materials. Compounds **3a–h** were subjected to exhaustive methylation in excess methyl iodide at room temperature for 1 week. Methyl iodide was then removed under vacuum, and the residue was washed several times with toluene and then with diethyl ether. The reaction was followed by TLC (silica, methanol/acetic acid 9:1). The mono- and bisalkylated fulleropyrrolidinium ions possess different values of R_f, 0.3 and 0.1, respectively. The products were characterized by ES-MS, where a peak at $m/2 = 564$ was the main peak (100%) in all cases. A minor peak at $m/z = 1128$ (M$^+$) was also present with intensity of about 5%, confirming the successful bisalkylation. The possible product of monoalkylation of the bis-adducts has a molecular weight of 1113, which was never observed in any of the bis-adducts used for the CV studies. All materials were reagent grade chemicals. TBAH (puriss from Fluka) was used as supporting electrolyte as received. Tetrahydrofuran (THF, LiChrosolv, Merck) was treated according to a procedure described elsewhere.[6] For the electrochemical experiments, the solvent was distilled into the electrochemical cell, prior to use, using a trap-to-trap procedure.

Electrochemical Instrumentation and Measurements. The one-compartment electrochemical cell was of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Viton O-rings to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck tube containing the solvent were obtained by spherical joints also fitted with Viton O-rings. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically 1.0 to 2.0×10^{-5} mbar. The working

electrode consisted either of a 0.6 mm-diameter platinum wire (0.15 cm^2 approximately) sealed in glass or of a Pt disk electrode (diameter 125 μm) also sealed in glass. The counter electrode consisted of a platinum spiral, and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ∼0.5 cm. Potentials were measured with respect to the ferrocene standard and are always referred to saturated calomel electrode (SCE). $E_{1/2}$ values correspond to (E_{pc} + E_{pa})/2 from CV. For irreversible peaks, the peak potential, E_p, is given, measured at 0.5 V s^{-1}. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple.

Voltammograms were recorded with a AMEL model 552 potentiostat or a custom made fast potentiostat[17] controlled by either a AMEL model 568 function generator or a ELCHEMA model FG-206F. Data acquisition was performed by a Nicolet model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda RL 6 CS thermostat.

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